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PHYSICAL PROPERTIES AND CHEMICAL REACTIVITY
OF ALTERNANT HYDROCARBONS
AND RELATED COMPOUNDS. XV.*

KINETICS OF THE DEDEUTERATION
OF BENZENOID HYDROCARBONS**

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The kinetics of the dedeuteration of a series of eight benzenoid monodeuterated hydrocarbons has been studied in the mixture trifluoroacetic acid (91.8 mol%)–perchloric acid (2.5 mol%)–water (5.7 mol%) at $30 \pm 0.1^\circ\text{C}$. A correlation has been found between the logarithms of the first-order rate constants ($\log k$) and HMO atom localization energies of the positions in hydrocarbons in which the deuterium atom is bound (A). There is a splitting of data into three groups according to the character of the position bearing the deuterium atom (*i.e.*, benzene-like, α -naphthalene-like, *meso*-anthracene-like positions). A similar correlation with SCF atom localization energies for electrophilic substitution (A_e^{SCF}), calculated according to Pople's procedure, has given only one regression line including all three types of positions. A comparison of the plots obtained with analogous plots for the dedeuteration in liquid hydrogen bromide (Šatenštejn) shows that the nature of the reaction remains unchanged in a solvent with a different dielectric constant.

The kinetics of the dedeuteration of some benzenoid hydrocarbons has been the subject of several papers in recent years²⁻⁸. Also, an extensive study devoted to the course of the deuteration of benzenoid hydrocarbons has been published⁹. Recently, Streitwieser and coworkers have reported the rates of deuterium-hydrogen exchange in the methyl group of methylarene- α - d 's^{10,11}.

The purpose of this paper is to present the results of a kinetic study of the deuterium-hydrogen exchange in monodeuterated benzenoid hydrocarbons.

* Part XIV: Tetrahedron, in the press.

** Presented at the 3rd Symposium on Stable Isotopes, Leipzig, October 28th–November 2nd, 1963. For a preliminary communication, see¹.

EXPERIMENTAL

MO Data

The values of Wheland atom localization energies of the respective positions in hydrocarbons (A) were taken from refs^{12,13}. The values of atom localization energies for electrophilic substitution calculated according to Pople (A_e^{SCF}) were taken from Chalvet¹⁴.

Compounds

Monodeuterated benzenoid hydrocarbons were synthesized in the usual manner by preparing the Grignard reagents or lithium compounds followed by hydrolysis of the organometallic with heavy water or acetic acid- d . Starting halides were either commercially available or were prepared according to published procedures. The melting points of monodeuterated hydrocarbons agreed with those reported. A list of experimentally studied compounds is given in Table I.

Heavy water used for the decomposition was of U.S.S.R. manufacture and had d_{25}^{25} 1.10781, 99.78 at. % D, specific conductivity $0.55 \times 10^{-5} \Omega^{-1} \text{ cm}^{-1}$. It contained 1.7 at. % of heavy oxygen isotopes. Acetic acid- d (CH_3COOD) was prepared from anhydrous acetic anhydride and heavy water.

Kinetic Measurements

Exchange experiments were performed in a mixture of 91.8 mol% CF_3COOH –2.5 mol% HClO_4 –5.7 mol% H_2O at $30 \pm 0.1^\circ\text{C}$. The sample of a deuterated hydrocarbon (usually 0.0004–0.0008 mol) was dissolved by shaking in 5 ml of the thermostated (30°C) acid mixture. When necessary, the solution was filtered through glass wool to remove undissolved crystals, and five aliquots of the final solution were transferred to tubes. These tubes were then sealed with glass stoppers and placed in the thermostated bath. The individual tubes were removed at appropriate intervals, neutralized by 5 ml of precooled 4N-NaOH (ice salt mixture), and extracted with 3–5 ml of chloroform. The chloroform solution was dried with anhydrous calcium chloride, filtered and evaporated to dryness. The dry residue obtained was analyzed for deuterium and in general the deuterium content in the last sample was one half to one third of that in the first sample.

In the case of benzene- d , the exchange reaction was performed with 0.5 ml benzene- d in 8 ml of the acid mixture. After reaction, neutralization, and extraction with 1 ml of chloroform, the chloroform solution was not evaporated and was used directly for the deuterium analysis.

Deuterium Analysis

Deuterium content in starting deuterated hydrocarbons was either determined after the combustion of the sample according to Horáček¹⁵, or by means of mass spectrometry. The degree of deuteration of the hydrocarbons was also checked on an infrared spectrometer UR-10 (C. Zeiss, Jena). The evaluation of kinetic runs was made by means of a mass spectrometer MCh 1303 (U.S.S.R.) with magnetic scanning and with an ionization energy of 12 eV.

Calculation of Rate Constants

Rate constants were calculated from the kinetic data according to the equation¹⁶,

$$k = (2.303/t) \log (D_0/D_t),$$

where k is the first-order rate constant for the deuterium–hydrogen exchange (s^{-1}), t is the time (s), D_0 is the deuterium content for the first sample removed ($t = 0$), and D_t that for a sample

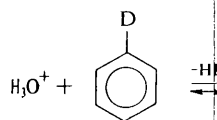
removed at time t .
in the sample would

Since the preparation of non-exchangeable deuterium, the amount of non-exchangeable deuterium in the sample at $t = 0$

The deuterium exchange rate constants were obtained from the correlation coefficient.

RESULTS AND DISCUSSION

The aromatic deuterium exchange. However, Gold and Gold¹⁷ found that the usual mechanism for most other aromatic compounds involves a rapid formation of a loose complex in a slow step to a transition state. The formation



The dedeuteration of aromatic mixtures as, e.g., sulfuric acid–water, bromide etc. With chloric acid (2.5 mol% in water) relatively soluble aromatic compounds can be studied.

A list of synthesized aromatic compounds and their order rate constants is given in Table II.

It is obvious that the hydrogen exchange reactivities with chloric acid assumptions¹⁸, the proposed mechanism is in agreement with the state I and the state II

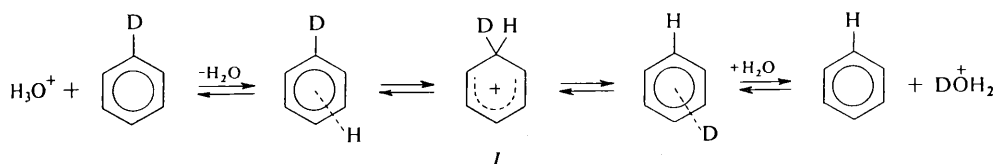
removed at time t . This equation was used under the assumption that the deuterium content in the sample would ultimately fall to zero at $t = \infty$.

Since the preparations of anthracene-1- d and anthracene 9- d contained a certain amount of non-exchangeable deuterium in the form of a dihydro derivative which was difficult to remove, the amount of non-exchangeable deuterium (obtained by the extrapolation of deuterium content in the sample at $t = \infty$) was subtracted prior to the calculation of the rate constant.

The deuterium exchange results were evaluated statistically and the mean values of the rate constants were obtained graphically. The values are summarized in Table I. Regression lines and correlation coefficients were calculated by the least squares method.

RESULTS AND DISCUSSION

The aromatic deuterium-hydrogen exchange is an electrophilic substitution reaction. However, Gold and Satchell¹⁷ suggested a more complex reaction mechanism than usual for most other electrophilic substitutions of aromatic systems. The exchange involves a rapid and reversible reaction of a proton with an aromatic substrate to form a loose "outer" complex of unspecified nature which is then transformed in a slow step to an analogous complex with reversed hydrogen and deuterium positions. The formation of this complex possibly occurs *via* the transition complex *I*:



The dedeuteration of benzenoid hydrocarbons has been studied kinetically in such mixtures as, *e.g.*, trifluoroacetic acid-perchloric acid-water, trifluoroacetic acid-sulfuric acid-water, aqueous sulfuric acid, sulfuric acid-acetic acid, liquid hydrogen bromide *etc.* We have chosen the mixture trifluoroacetic acid (91.8 mol%)-perchloric acid (2.5 mol%)-water (5.7 mol%) at 30°C, in which the hydrocarbons are relatively soluble and the exchange rates were acceptable for all compounds under study.

A list of synthesized deuterated hydrocarbons and the logarithms of the first-order rate constants of deuterium-hydrogen exchange are summarized in Table I.

It is obvious that monodeuterated benzenoid hydrocarbons and their deuterium-hydrogen exchange reaction represent a suitable series for a correlation of relative reactivities with quantum-chemical reactivity indices. Under usually accepted assumptions¹⁸, the logarithm of the rate constant of deuterium-hydrogen exchange ought to be proportional to the π -electronic energy difference between the transition state *I* and the starting benzenoid hydrocarbon. This difference is defined as equal

TABLE I
Monodeuterated Benzenoid Hydrocarbons and the Rate Constants of Their Dedeuteration

No	Compound	Class	Mol. formula	Sample No	At. % D calculated (found) ^a	Degree of deuteration, %
1	Benzene- <i>d</i>	0	C ₆ H ₅ D	— I II	16.67 (16.08) (14.05)	— 96.4 84.3
2	Naphthalene-1- <i>d</i>	1	C ₁₀ H ₇ D	— I II	12.50 (10.55) (10.42, 10.53)	— 84.4 83.4, 84.3
3	Naphthalene-2- <i>d</i>	0	C ₁₀ H ₇ D	— I II III	12.50 (5.01) (7.00) (3.35)	— 40.1 56.0 26.8
4	Anthracene-1- <i>d</i>	1	C ₁₄ H ₉ D	— I	10.00 (6.08) ^{h,i}	— 60.8 ^{h,i}
5	Anthracene-9- <i>d</i>	2	C ₁₄ H ₉ D	— I II	10.00 (8.83) (2.51) ⁱ	— 88.3 25.1 ⁱ
6	Phenanthrene-9- <i>d</i>	1	C ₁₄ H ₉ D	— I	10.00 (4.49, 4.48)	— 44.9, 44.8
7	Biphenyl-2- <i>d</i>	1	C ₁₂ H ₉ D	— I	10.00 (6.46)	— 64.6
8	Biphenyl-3- <i>d</i>	0	C ₁₂ H ₉ D	—	10.00	—
9	Biphenyl-4- <i>d</i>	0	C ₁₂ H ₉ D	— I II III	10.00 (6.69) (4.74) (5.87)	— 66.9 47.4 58.7

^a The analyses in italics were made by the method of Horáček¹⁵, all other analyses mass-spectrometrically. ^b From the corresponding halide, A: via Grignard reagent, D₂O used for the decomposition; B: via Grignard reagent, CH₃COOD used for the decomposition; C: via lithium derivative, CH₃COOD used for the decomposition. ^c 91.8 mol% CF₃COOH–2.5 mol% HClO₄–5.7 mol% H₂O, at 30 ± 0.1°C. The dielectric constant for CF₃COOH is 39.5 (at 20°C), for water the values are 80.36 (at 20°C) and 76.75 (at 30°C). No value of the dielectric constant could be found for HClO₄; for the solvent mixture used, the estimated value of the medium is approximately

TABLE I
(Continued)

Method of preparation ^b	M. (b.)
—	—
A	n _D ²⁰
B	n _D ¹⁵
—	79.5
A	—
B	—
—	80
A	—
B	—
C	—
—	213
C	—
—	213
A	—
C	—
—	9
B	—
—	68
B	—
—	68.5
—	—
A	—
A	—
A	—

43 (at 20°C). ^d Liquid constant of HBr is 1.5. ^e SCF-MO atom loc. ^f n the number of kinetic units. ^g 6.60% anthracene-*d*₂ and 94.40% anthracene-*d*₁ only. ^h The assignment of results, see Exp

ants of Their Dedeuteration

% D calculated
(found)^a

Degree of
deuteration, %

16.67 (16.08) (14.05)	— 96.4 84.3
12.50 (10.55) (10.42, 10.53)	— 84.4 83.4, 84.3
12.50 (5.01) (7.00) (3.35)	— 40.1 56.0 26.8
10.00 (6.08) ^{h,i}	— 60.8 ^{h,i}
10.00 (8.83) (2.51) ⁱ	— 88.3 25.1 ⁱ
10.00 (4.49, 4.48)	— 44.9, 44.8
10.00 (6.46)	— 64.6
10.00	—
10.00 (6.69) (4.74) (5.87)	— 66.9 47.4 58.7

TABLE I
(Continued)

Method of preparation ^b	M.p., °C (b.p., °C)	log <i>k</i> , s ⁻¹		<i>A</i> (-β) ^e	<i>A</i> _c ^{SCF} eV ^f	<i>n</i> (<i>m</i>) ^g
		solvent A ^c	solvent B ^d			
—	(80°)	-5.81 ± 0.01	-7.30	2.536	25.715	2 (10)
<i>A</i>	<i>n</i> _D ²⁰ 1.5004					
<i>B</i>	<i>n</i> _D ¹⁵ 1.5053					
—	79.5—80.5°	-3.12 ± 0.01	-2.60	2.299	24.643	2 (10)
<i>A</i>						
<i>B</i>						
—	80—80.5°	-4.06 ± 0.02	-4.30	2.479	25.199	2 (10)
<i>A</i>						
<i>B</i>						
<i>C</i>						
—	213—214°	-2.53	—	2.230	24.213	1 (3)
<i>C</i>						
—	213—214°	-1.58 ± 0.04	—	2.013	23.502	2 (5)
<i>A</i>						
<i>C</i>						
—	99.5°	-3.10 ± 0.02	—	2.299	24.497	3 (13)
<i>B</i>						
—	68—69°	-4.03 ± 0.02	-4.59	2.400	24.889	2 (8)
<i>B</i>						
—	—	—	< -7.7	2.544	25.513	—
—	68.5—69°	-4.00 ± 0.01	-3.85	2.447	24.940	2 (10)
<i>A</i>						
<i>A</i>						
<i>A</i>						

all other analyses mass-spectro-
gent, D₂O used for the decom-
position; *C*: via lithium deriva-
CF₃COOH-2.5 mol% HClO₄-
OH is 39.5 (at 20°C), for water
the dielectric constant could be
of the medium is approximately

43 (at 20°C). ^d Liquid hydrogen bromide, at 25°C, the data were taken from ref.⁸. The dielectric
constant of HBr is 3.82 (at 24°C). ^e Wheland atom localization energy, HMO, see^{12,13}.
^f SCF-MO atom localization energy for electrophilic substitution, according to the ref.¹⁴.
^g *n* the number of kinetic runs, *m* the number of analyzed samples. ^h The product also contained
6.60% anthracene-*d*₂ and 3.41% anthracene-*d*₃. The analysis given in Table I concerns anthra-
cene-*d* only. ⁱ The amount of non-exchangeable deuterium was subtracted prior to the evalua-
tion of results, see Experimental.

to the Wheland localization energy of the position in the parent benzenoid hydrocarbon bearing the substituent (*i.e.*, deuterium). It can be seen from the plot of $\log k$ values against Wheland atom localization energies A (Fig. 1) that there exists a correlation. As splitting into three classes can be observed depending on the type of position bearing the deuterium atom (benzene-like, α -naphthalene-like, *meso*-anthracene-like positions)¹². However, the splitting into three classes is not statistically significant because of a *small number of data* in the respective classes. Nevertheless, in spite of the small number of data, we assume that there is a splitting because a statistically significant splitting has been found in the case of electrophilic deuteration, nitration, and bromination¹⁹.

We intended to study the kinetics of dedeuteration also in another medium with a different dielectric constant where the reaction mechanism would be the same. However, the exchange reaction was too slow both in the mixture acetic acid-sulfuric acid (mol. ratio 50 : 1)⁶ and in the mixture trichloroacetic acid-sulfuric acid-water. Therefore, we used kinetic data obtained by Šatenštein and coworkers⁸ for the deuterium-hydrogen exchange in liquid hydrogen bromide. We were able to establish a similar character of the plot of $\log k$ vs. A as in the previous case even when the number of data in the respective classes was small (Fig. 2).

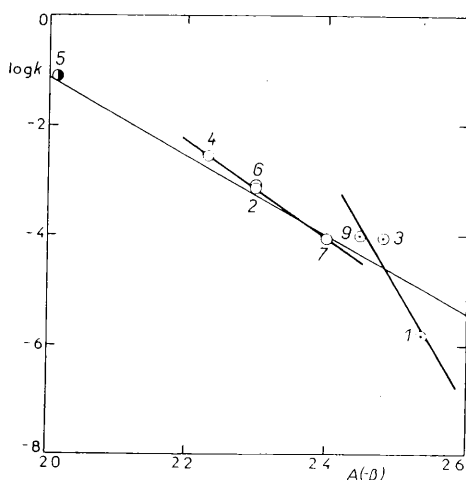


FIG. 1

Plot of $\log k$ of the Dedeuteration of Benzenoid Hydrocarbons in the Mixture $\text{CF}_3\text{COOH}-\text{HClO}_4-\text{H}_2\text{O}$ at 30°C against Wheland HMO Atom Localization Energy A

For designation of compounds, see Table I; classes: 0 (benzene-like) ○, 1 (α -naphthalene-like) ●, 2 (*meso*-anthracene-like) ◐. Thin line: a common regression line for the three classes, $\log k = -7.087A (-\beta) + 13.039$, correlation coefficient $r = 0.939$, number of compounds $n = 8$, all data are significant on 1% probability level.

When self-con
 A_6^{SCF} , based on
a single regressi
linear relations
As expected, on
vs. analogous va

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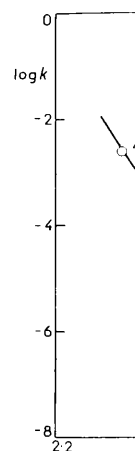


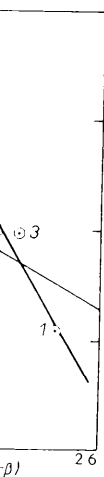
FIG. 2

Plot of $\log k$ of the Dedeuteration of Benzenoid Hydrocarbons in the Mixture $\text{CF}_3\text{COOH}-\text{HClO}_4-\text{H}_2\text{O}$ at 30°C against Wheland HMO Atom Localization Energy A

For designation of compounds, see Table I; classes: 0 (benzene-like) ○, 1 (α -naphthalene-like) ●, 2 (*meso*-anthracene-like) ◐. Thin line: a common regression line for the three classes, $\log k = -7.087A (-\beta) + 13.039$, correlation coefficient $r = 0.939$, number of compounds $n = 8$, all data are significant on 1% probability level.

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hydrogen bromide. We were able to
s. A as in the previous case even
as small (Fig. 2).



carbons in the Mixture CF_3COOH -
tion Energy A
on line for the three classes, $\log k =$
939, number of compounds $n = 8$,

When self-consistent values of localization energies for electrophilic substitution¹⁴, A_e^{SCF} , based on the Pople-type of SCF calculation, were used for the correlation, a single regression line including all the three classes was obtained (Fig. 3). Similar linear relations $\log k$ vs. A_e were obtained previously by Dewar and Thompson²⁰. As expected, one regression line was obtained in the plot of our dedeuteration data vs. analogous values for deuteration⁹ (Fig. 4).

The splitting of data into three groups according to classes in the case of correlations with HMO localization energies is typical for all electrophilic substitutions occurring on the skeleton; in the case of radical substitutions only one regression line was obtained. An explanation of this has been published recently¹⁹. A plot of SCF localization energies for polar substitutions against HMO localization energies shows an analogous splitting of data into three groups which resembles that for the dependences of logarithms of rate constants, whereas the plot for SCF radical localization energies gives one regression line only. In polar substitutions the π -electronic contribution to the activation energy equals the difference between π -electronic

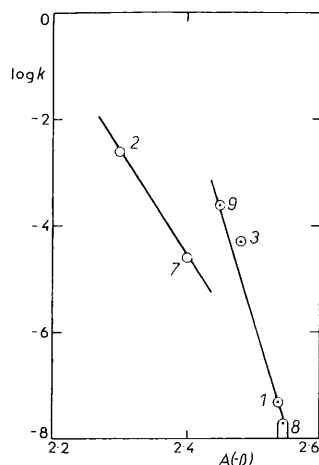


FIG. 2

Plot of $\log k$ of the Dedeuteration of Benzenoid Hydrocarbons in Liquid Hydrogen Bromide at 25°C (see⁸) against Wheland HMO Atom Localization Energy A

For designation of compounds, see Table I, the classes are the same as in Fig. 1.

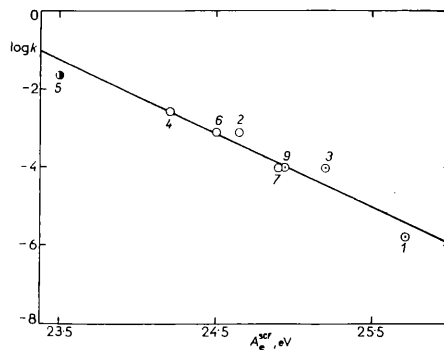


FIG. 3

Plot of $\log k$ of the Dedeuteration of Benzenoid Hydrocarbons in the Mixture $\text{CF}_3\text{COOH-HClO}_4\text{-H}_2\text{O}$ at 30°C against SCF-MO Atom Localization Energy A_e^{SCF} (see¹⁴)

For designation of compounds, see Table I. $\log k = -1.851A_e^{\text{SCF}}(\text{eV}) + 42.201$, $r = 0.977$, $n = 8$, all data are significant on 1% probability level.

energies of a charged and uncharged particle, in the case of a radical substitution it is a difference of π -electronic energies of two uncharged particles. Because the electronic repulsion is different in positions of different classes, it is impossible to get a simple linear dependence for a polar substitution when HMO localization energies are used for the correlation. On the other hand, one regression line can be obtained when SCF localization energies are used.

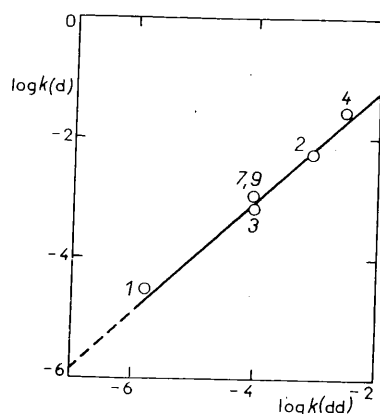


FIG. 4

Plot of $\log k$ of Deuteration (for reaction conditions, see⁹) against $\log k$ of Dedeuteration of Benzenoid Hydrocarbons in the Mixture $\text{CF}_3\text{COOH}-\text{HClO}_4-\text{H}_2\text{O}$ at 30°C

The value for the compound 5 is omitted. For designation of compounds, see Table I. $\log k$ (deuteration) = $0.883 \log k$ (dedeuteration) + 0.584 , $r = 0.996$, $n = 6$, all data are significant on 1% probability level.

It follows from the comparison of the data obtained in the mixture trifluoroacetic acid-perchloric acid-water as well as in liquid hydrogen bromide (the corresponding dielectric constants are approximately 43 for the mixture and 3.82 for hydrogen bromide) that the nature of the dependences remains about the same, in spite of the difference between the dielectric constants of both media.

The mechanism of the dedeuteration of benzenoid hydrocarbons in basic solutions (potassium amide in liquid ammonia or lithium cyclohexylamide in cyclohexylamine)^{7,8,10,11,21} is different and attempts to correlate the logarithms of rate constants with HMO quantum-chemical reactivity indices are more complicated.

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M. Řežábková for her careful